Terminal solid solubility of hydrogen in Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe

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1. Introduction

Zr-based alloys have been widely used as fuel cladding for light water reactors because of their low neutron absorption cross section and good corrosion resistance. Hydrogen, generated mainly from the oxidation reaction between Zr alloy and cooling water is absorbed into the claddings. When the hydrogen concentration in Zr alloys exceeds the terminal solid solubility(TSS), the claddings are susceptible to a crack initiation and a propagation. Therefore, an accurate value of the TSS is an important factor in the Zr-based alloy. There are many reports about the terminal solid solubility of hydrogen during a heatup and cooldown with various techniques. The purpose of this study is to determine the terminal solid solubilities of hydrogen during the dissolution of a hydride at a heatup and during the precipitation of hydrides at a cooldown in Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe by using a DSC and to study the effect of the alloy on the hydrogen solubility by comparing the values between Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe.

2. Experimental

Hydrogen was introduced into Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe specimens by two methods. One was a gas charging at 400 ℃ in an Ar/H2 mixed gas, and the absorbed hydrogen concentrations were controlled by varying the reaction duration. The other was a electrolyte cathodic charging. A platinum anode and an electrolytic of 10vol.% H_2SO_4 + 90vol.% H_2O were used for the cathodic charging. Then the specimens were annealed in separated quartz tubes, sealed under a vacuum, at 673K for 24h to make sure that the hydrogen concentration was uniform within the specimens. The specimens were measured by using a differential scanning calorimeter (Netzsch DSC-404) to obtain the hydride dissolution /precipitation temperature. Each specimen was measured for the hydride dissolution/precipitation temperature in three consecutive thermal cycle runs. The mean of the last two results of the three runs was chosen to be a result because the first run was affected by the prior thermal history. The DSC measurements were carried out in purified Ar at a flow rate of 50 cm^3 /min. In all the measurements, the maximum temperature was chosen to be 600℃ and the coldown/heatup rate was 10℃/min. The hydrogen concentration of the specimens was analyzed after the DSC measurements by the hot vacuum extraction method with an accuracy of ± 3%.

3. Results and Discussion

A typical DSC curve with its time deviation(DDSC) for Zircaloy-4 containing 246ppm hydrogen, obtained during a heatup is given in Fig.1. In the figure, endothermic peaks relative to a baseline are detected in the range of 200 - 450℃. This is from a hydride dissolution. The heat flow increases with a increasing temperature as the heat is absorbed by the specimen to dissolve the hydrides. In our analyses, the maximum slope point of the heat flow curve was adopted as the TSSD temperature based on a good reproducibility and on a good agreement with previously reported equilibrium TSSD data[1]. Some authors chose the peak temperature of the DSC for the TSSD. There are no rules for a temperature which best represents the temperature for a complete hydride dissolution. The DSC curve obtained on a cooldown for Zircaloy-4 containing 246ppm hydrogen is given in Fig.2. A similar procedure was also followed to analyze the cooldown data. Both alloys show hysteresis effects between the terminal sold-solubility limits obtained from the heating curves and the cooling curves due to a volumetric misfit strain between the Zr matrix and the less dense hydride phases[2-3].

The logarithms of the solubilities in ppm hydrogen by weight are plotted against the inverse of the absolute temperature in Fig. 3. The terminal solid-solubility results in Fig. 3 show no difference for Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe and are in good agreement with previous results [1,4,5] that low alloy additions do not influence the solubility of the hydrogen.
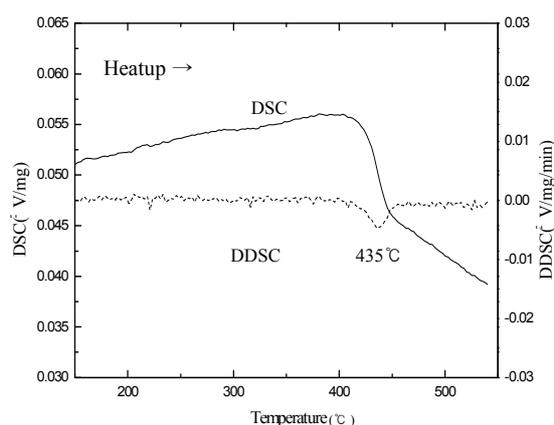

Fig. 1. DSC data from Zircaloy-4 containing 246ppm hydrogen, obtained during a heatup.
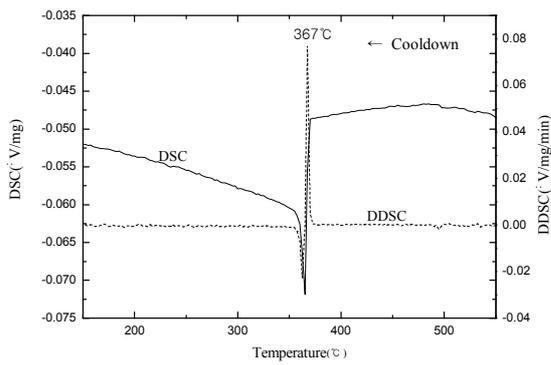
Fig. 2. DSC data from Zircaloy-4 containing 246ppm hydrogen, obtained during a cooldown.
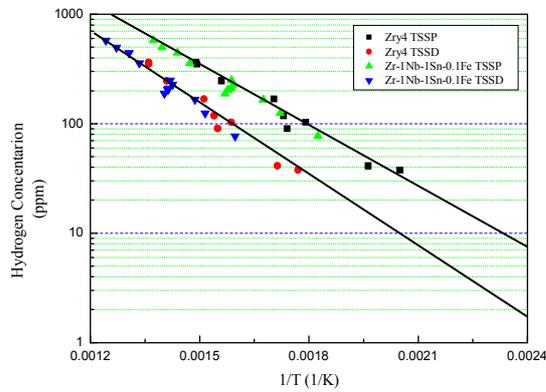

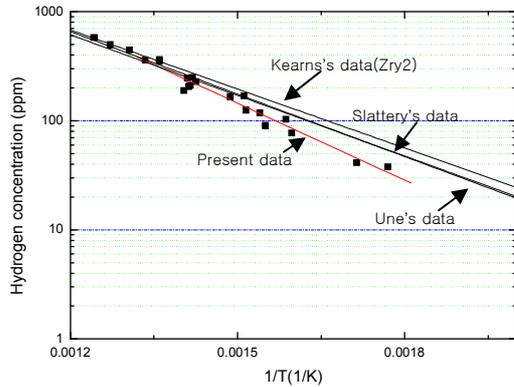Fig. 3. TSSD and TSSP for hydrogen in Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe.

Fig. 4. Comparision of present and literature TSSD solvi obtained for Zr, Zircaloy-2 and Zircaloy-4

The best-fit lines through the present data for the Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe can be represented by the following equations :

$$C_{TSSD} (ppm) = 4.93*10^5 \exp(-45087/RT)$$
$$C_{TSSP} (ppm) = 1.47*10^5 \exp(-34117/RT)$$

where R is the gas constant(8.314J/K/mol) and T, the temperature in K.

Fig. 4 compares the present and literature TSSD solvi obtained for Zr, Zircaloy-2 and Zircaloy-4. The present activation energy for the hydride dissolution is 45kJ/mol. The data level of the present study is smaller than Kearn's data[4] which has been sometimes refered to as an equilibrium phase boundary for hydrogen in the α phase and the latest data of Une[5] which were investigaeted by the same technique(DSC).

In the comparisions of the present and other TSSP data, a large scatter was seen in the TSSP solvi for each investigation. It may result from a non-equilibrium or path-independent character of the TSSP. This present activation energy for the hydride precipitation is 34 kJ/mol and other investigatiors have reported values of 21-34 kJ/mol.

4. Conclusion

The terminal solid solubilities of hydrogen during the dissolution of a hydride(TSSD) at a heatup and during the precipitation of hydrides(TSSP) at a cooldown were determined for Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe by using a DSC. The minor differences in the alloying elements between the Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe creates no difference in the terminal solubility.

The present activation energies for the hydride dissolution and precipitation are 45kJ/mol and 34kJ/mol, respectively. The data level of the present study is smaller than Kearn's data which has been sometimes refered to as an equilibrium phase boundary for hydrogen in the α phase and the latest data of Une which were investigated by the same technique(DSC).

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